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Two way diffusion model for the recording mechanism in a self developing dry acrylamide photopolymer

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ABSTRACT

In our most recent study[1] diffusion constants were measured in the simplified monoacrylamide version of a dry acrylamide based photopolymer holographic recording material developed in the Centre for Industrial and Engineering Optics. In this paper we report diffusion constants for the commonly used photopolymer formulation, which also contains the crosslinker bisacrylamide. A physical model for the recording mechanism is proposed which explains the two way diffusion observed in both systems, and is in agreement with much of the previously observed behaviour of the material, particularly in regard to dependence of diffraction efficiency growth on spatial frequency and persistence of holographic gratings under uniform exposure. The model is also supported by direct observation, under a surface profiler, of the boundary between an illuminated and un-illuminated area at the photopolymer surface.

1. INTRODUCTION

Photopolymer holographic recording media have been the focus of increasing attention of late because of their high sensitivity, large dynamic range, easy processing and relatively low cost. Photopolymerizable systems, because of the amplification afforded by the chain reaction that polymerization entails, generally have greater sensitivity and diffraction efficiency. Development of dry self-processing photopolymerizable systems[2], makes photopolymers suitable for a large variety of applications – design of optical elements[3,4] , real-time interferometry[5,6] and write once optical memories[7-9]. The acrylamide-based photopolymer, published by Calixto[10], and developed in our laboratory[11,12] has excellent characteristics for transmission hologram recording and is beginning now to show significant potential for reflection holography. A typical growth curve for the diffraction efficiency of a grating (monitored in real time during recording) is shown in Figure 1 (previously published in Ref.13). In this example the diffraction efficiency approaches 100% and then decreases, due to overmodulation (i.e. further increase in the refractive index modulation), as the diffracted light is coupled back into the zero order. This shows the ease with which highly efficient gratings can be recorded.

A disadvantage of this photopolymer system in the formulation discussed here is its poor response at high spatial frequency holographic recording. This is one of the main stumbling blocks in the way of good reflection holography, although shrinkage[14], however small, may also be problematic in reflection mode of recording. To improve the high spatial frequency response and/or shrinkage, a thorough understanding of the holographic recording mechanism in this particular system was required. Because the grating develops immediately in this material, its diffraction efficiency can be monitored during recording. As seen above, the material has a good dynamic range and for relatively short exposure times, gratings of close to 100% efficiency can easily be recorded, even at low spatial frequency. The recorded gratings (in the crosslinked formulation) are stable for months without protection from the environment, and if sealed will maintain their diffraction efficiency for years. In normal recording of gratings the growth of the grating stops sharply as soon as the illumination is stopped and diffraction efficiency does not fall significantly. However, in the non crosslinking formulation there is a decrease in the diffraction efficiency which causes the grating to disappear within days or hours of recording. In order to understand and improve this material we need a model for the mechanism of holographic recording which can explain the growth of the grating during normal recording, the disappearance of gratings in the acrylamide-only formulation and the limits to material resolution

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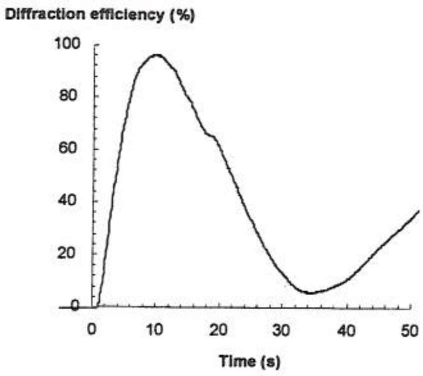


Fig. 1. Diffraction efficiency as a function of exposure time for a 300 lines/mm grating recorded with a total intensity of $4mW/cm^2$ (previously published in Ref.13)

Theoretical models describing holographic grating formation in different photopolymer systems predict that the monomer diffusion rate is a crucial factor during holographic recording. This prompted our recent work on character-rization of diffusion properties of this material, which is continued here. We recently presented[1] the first independent measurements of the diffusion constants characterizing the diffusion processes in the dry acrylamide–based photopolymer system. Here we report results for the full optimized photopolymer system, which also contains the crosslinker bisacrylamide. This allows us to propose a physical model for the recording mechanism in the material, which we describe below.

Diffusion

Diffusion models[15-20] predict that the key factor that controls dynamics and final properties of the recorded holographic grating (refractive index space profile and modulation) is the ratio of polymerization rate and monomer diffusion rate. At any given spatial frequency, two different regimes of holographic recording can be distinguished depending on whether the diffusion rate or the polymerization rate is the faster process. When the polymerization rate is slower than the diffusion rate, the grating profile closely resembles a sinusoidal recording interference pattern. When the monomer diffusion rate is slower than the polymerization rate deviation from the sinusoidal profile of the grating is observed and the diffraction efficiency at saturation is lower. The monomer diffusion rate is characteristic for a given photopolymer system. There is little data available for diffusion constants in photopolymer systems. The monomer diffusion rates that have been measured are relatively slow (6.51×10^{-11} cm^2/s for Omnidex DuPont photopolymers[19] and 3.57×10^{-14} cm^2/s for the system investigated by Colvin et al[18]). Figures published for diffusion constants in acylamide based photopolymers similar to this one are also slow ($3.31x10^{-14}cm^2/s$)[20]. However, it should be borne in mind that modeling the diffraction grating kinetics in continuous mode can only supply information about the ratio of polymerization and diffusion rates, and the accuracy of the diffusion constant obtained in that way depends on the polymerization rate used. Given that much of the published data relates to DuPont's photopolymer, it is unwise to make assumptions about polymerization rates and/or diffusion rates in this material based on measurements made in very different materials. Where separate experimental measurements of polymerization and diffusion rates can be made, it is important to do so.

In a previous paper[1] we carried out a separate determination of the diffusion rate in an acrylamide based material. This was done using the method described by Colvin et al, increasing the recording intensity so that the polymerization rate was faster than the diffusion rate, and using short exposure time for recording holographic gratings with low diffraction efficiency (of the order of 1%). We were able to distinguish and quantify two diffusion processes which make opposing contributions to the final diffraction efficiency in a simplified version of the material formulation (acrylamide only, no crosslinker). The diffusion coefficient for the first process was $D_0=1.61 \pm 0.03\times10^{-7}cm^2/s$, and for the second $D_0= 6.35 \pm 0.2 \times10^{-10}$ cm^2/s. This paper describes the continuation of this work in the more stable standard crosslinking formulation used in holographic recording and reports new diffusion constants for both processes. A physical model for the recording mechanism is proposed which helps explain these two diffusion processes, as well as other characteristics of this photopolymer material.

2. EXPERIMENTAL

2.1. Materials

The photosensitive layer was prepared as previously described[1]. Briefly, 2ml of triethanolamine was added to 17.5ml stock solution of polyvinyl alcohol (PVA) (10% w/w). Then the monomers, 0.32g – N,N methylene bisacrylamide and 0.48g acrylamide, were added. Finally, 4ml of erythrosin B dye was added (stock solution concentration - 1.1mM). The solution was made up to 25ml by adding distilled water. 2ml of this solution were spread on a 50x50mm plate. The samples were dried for 36 - 48 hours. Sample thickness after drying was approximately 150μm.

2.2. Dynamic measurement of diffraction efficiency

As the response of these materials to light is immediate, the diffraction efficiency can be measured during the grating /hologram recording. This is done using a 633nm Helium Neon laser source with a 1mm unexpanded beam incident upon the grating at the Bragg angle for 633nm light. The diffracted light is then monitored by a photodetector, whose signal is recorded by a PC controlled data acquisition system.

2.3. Measurement of monomer diffusion coefficient

The method described by Colvin et al[18] was again utilized to measure the monomer diffusion coefficient. The growth of the diffraction efficiency in a transmission grating was recorded during and after a very short exposure (the recording time needs to be faster than the expected monomer diffusion time). The exposure was chosen to be small enough so that the diffusion coefficient could be assumed not to be spatially modulated. Transmission gratings were recorded using a $NdYVO_4$ laser (Verdi 05) 532nm and recording times were in 0.1-2 s range. Diffraction efficiencies were of the order of a few percent. The refractive index modulation was monitored as described elsewhere[1] and the curves representing the time dependence of the refractive index change were fitted with Microcal Origin software applying the Levenberg–Marquardt method for minimizing the chi-square value. The diffusion time τ_d at given spatial frequency was extracted from the fitting results. Using the relation[17,19]

$$\tau_d = 1/D_0K^2, \qquad (1)$$

where $K=2\pi/\Lambda$, and Λ is the fringe spacing, after linear fit of the diffusion time dependence on $1/K^2$, the diffusion constant D_0 was calculated.

2.4.Fitting procedure

In order to extract the time constants for the two processes observed after short illumination, initially we used a two exponential fit – one exponent with negative amplitude to describe the rising component and one with positive amplitude for the decaying component. This approach proved to give unsatisfactory results for this system despite having worked well for the system containing one monomer reported in Ref.1. It was not surprising that in the one-monomer system the first process was well fitted by a single exponent, since this rising component is ascribed to monomer diffusion. The fact that the decaying component was also well fitted by single exponent, implies that either the polymer chains formed during this short exposure have similar length or that only polymer chains with size below a given limit participate in this second diffusion process. Certainly there is significant homogeneity of the diffusing species. In the absence of crosslinker the polymer chains are expected to grow linearly, however, as already mentioned above, the picture significantly changes when a crosslinker is added. The main difference between the new system and the containing one monomer is the heterogeneity of the diffusing species, as there is now more than one monomer present. This is also true for the second diffusion process as the crosslinked polymer chains may differ greatly from each other in size. Presumably there is also a significant restriction on diffusion of individual chains related to the degree to which different growing chains are interwoven with one another in the crosslinking process. In order to reflect this heterogeneity we adopted the approach previously used by Veniaminov and Bartsch[21]. We used a stretched exponential function in fitting our experimental data:

$$y = A_1 \exp(-t/\tau_1)^{\beta_1} + A_2 \exp(-t/\tau_1)^{\beta 2}, \qquad (2)$$

Where τ_i are the time constants characteristic for the two processes, and they are related to the diffusion coefficient D_i through equation (1). A_i is the amplitude and it is negative for the first process leading to diffraction efficiency growth, and it is positive for the second diffusion process leading to diffraction efficiency decay. The stretching parameter βi is a measure of the heterogeneity of the diffusing species. Usually the larger the deviation of β from 1 the more heterogeneous is the characterized system or process. β was typically 0.5 for the first process and 0.2 for the second one indicating, as might be expected, that the monomer diffusion is the more homogeneous process of the two.

2.5. White light Interferometer measurements

A MicroXam Phase shifting White Light Interferometer was used to obtain the height profiles of the photopolymer surface. The system has a vertical resolution of 1nm in phase shifting mode, and a maximum lateral resolution of the order of 3 microns (depending on the magnification used).

3. RESULTS AND DISCUSSION

3.1. Diffusion constants for crosslinking formulation

The diffusion constants for crosslinking formulation (acrylamide and N,N methylene bisacrylamide in 3/2 weight ratio) are calculated from the data obtained by dynamic measurement of the diffraction efficiency, after very short exposures. Figure 2 shows the typical behaviour of the diffraction efficiency (on Bragg) after the illumination is abruptly stopped (Laser off arrow) at three different spatial frequencies. The diffraction efficiency rises rapidly at first (post-exposure process 1) and then falls off slowly (post-exposure process 2). There is a clear dependence on the spatial frequency. This dependence was also observed at different ratios of crosslinker (bisacrylamide) to monomer (acrylamide).

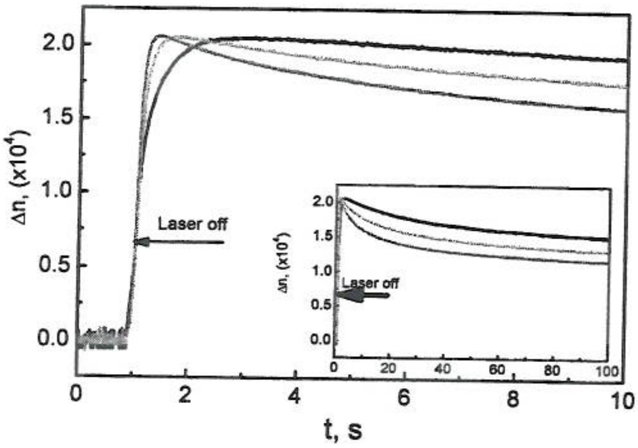


Fig. 2 Spatial frequency dependence of the refractive index modulation after recording for 0.2s with intensity 10mW/cm2 at 200 l/mm (black), 350 l/mm (light gray) and 500 l/mm (gray).

It was found that both the rising component of the curve, that occurs immediately after the exposure has ended, and the falling component that follows, could be fitted using stretched exponential functions and a time constant extracted as explained above. The time constants were then plotted against the inverse of the square of the fringe spacing in order to obtain the diffusion constants. Figures 3 and 4 show these plots for the rising (PP1) and falling (PP2) curves respectively. These graphs give us the diffusion constants, but the most important conclusion to be drawn from this data is that the time constants for both processes clearly show a strong dependence on the spatial frequency at this range of spatial frequencies. This is strong evidence for the proposal that the rise in diffraction efficiency observed after exposure ends (PP1) and the subsequent fall-off (PP2) are *both* diffusion processes. A possible alternative explanation would be that the rise is a continuation of polymerization processes. However, this would not account for the spatial frequency dependence we have observed, which has been repeated many times obtaining the same straight line It is shown below that there is other evidence that both processes are diffusion processes. The first post-exposure process (PP1) can be easily explained by attributing it to the influx of monomer which, it is widely accepted, occurs as a result of the concentration gradients set up by the polymerization process. If the main contributor to the grating refractive index modulation is density change (see below) then a further influx of monomer would increase the local density and increase the diffraction efficiency.

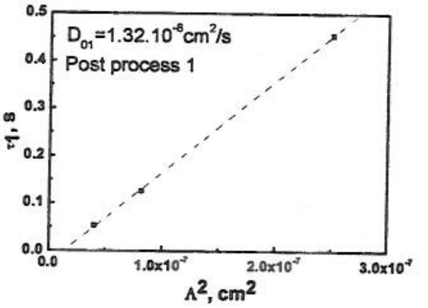


Fig. 3. The time constant obtained for post process 1 plotted as a function of the square of the grating fringe spacing

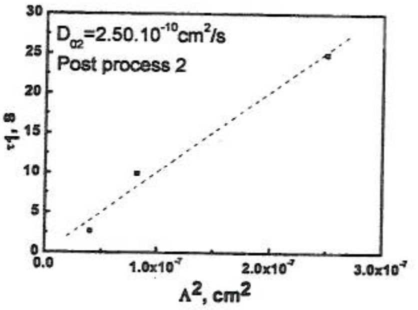


Fig. 4. The time constant obtained for post process 2 plotted as a function of the square of the grating fringe spacing

The deterioration that is subsequently observed in the second process is clearly also a diffusive process that, by some mechanism, reduces the density modulation achieved during the initial exposure. Since it is a diffusive process, the reduction in refractive index modulation can only be due to movement of material out of the bright fringe regions. Influx of some lower density material would not reduce local refractive index modulation unless it is displacing a higher density material, so the movement of some material out of the bright fringe regions must be occurring.

3.2. Two way diffusion mechanism

In the existing literature, authors attempting to model recording mechanisms[20] attribute resolution limits to non-local polymerization, meaning broadening of the polymerising area due to the growth in size of polymer molecules and generally it is assumed that polymer molecules remain located where they are formed. This doesn't account for the continuation of the grating deterioration which in some cases continues for hours and days after exposure has ended, nor for the diffusion processes observed above. We propose an alternative model where the diffusion of polymer molecules into the neighbouring region is considered. We propose that in this material, which has long been considered particularly permeable[22] polymer chains can diffuse away from the bright fringe areas and thereby reduce the refractive index modulation. The other limitation with existing models is that they depend primarily on the ratio of polymerisation o diffusion. With two unknowns, the data fits become less reliable. Recent papers have shown that in fact these models an be made to fit a broad range of disparate results by simply changing the assumed polymerisation or diffusion rates[23]. n order to extract reliable information by fitting with these theoretical models, one needs to characterize separately at east one of the crucial parameters – diffusion or polymerization rate, and, even more importantly, to take into account heir time evolution as more and more of the system is polymerized. We have now independently measured the "dark"[1] iffusion constants in our material and have recently published independently measured polymerisation rates also[24].

Figure 2, which is a typical example of the type of measurements taken during the above diffusion study, can now be interpreted as follows. During exposure polymerisation occurs in the bright fringe regions and monomer begins to diffuse in from the dark fringe regions. At the same time, as soon as a sufficient concentration gradient of polymer has built up, polymer begins to diffuse back into the dark fringe regions. The point at which the illumination is stopped is indicated by the 'laser off' arrow. The diffraction efficiency continues to grow because, despite the fact that no new polymer chains are being initiated, diffusion of monomer, which had lagged behind polymerisation slightly, continues to occur, until the concentration gradient disappears. Meanwhile, the loss of polymer back into the dark fringe regions is also occurring but at a slower pace, as the molecules are much larger. At some point the rise in diffraction efficiency caused by the diffusing monomer (PP1) is overtaken by the fall in diffraction efficiency caused by the movement of polymer, and a fall off in efficiency (PP2) is observed. It should be noted that PP1 and PP2 are not usually observed separately during normal recording, because the time scale is generally longer. These measurements have been taken after short, high intensity exposure so that we are working in the regime where polymerisation processes are faster than diffusion. As can be seen from the following table, the constants measured are also greatly affected by the presence of crosslinker.

Diffusion Constant	Without crosslinker	With crosslinker
For PP1 (rise)	$1.61 \times 10^{-7} cm^2/s$.	$1.32 \times 10^{-8} cm^2/s$.
For PP2 (fall)	$6.35 \times 10^{-10} cm^2/s$	$2.50 \times 10^{-10} cm^2/s$.

The three conclusions that can be drawn from the above work are that diffusion is fast in this material, crosslinker restricts the diffusion processes, and both PP1 and PP2 are diffusion processes. It is not so surprising that this material would have a very different diffusion constant to the DuPont material which is not prepared with aqueous chemicals and whose constituents differ greatly from those of this material. When the behaviour (growth curves, speed of DE development) of the DuPont material is compared to the material developed at IEO's laboratories all the indications are that the latter material has much faster diffusion. For example, in our material the full diffraction efficiency grows immediately upon recording. The growth curve, as explained below, is generally smooth, and the response (in the basic formulation discussed in this paper) is not as good at higher spatial frequency.

3.3. Evidence for two way diffusion in observed behaviour:

It is useful to examine observed behaviour and characteristics of this material in the context of two way diffusion and to examine the evidence for the above explanation.

a) Existence of two distinct and opposite diffusion processes.

As demonstrated above and in many similar experiments, there is a strong dependence of PP1 and PP2 on the grating spacing. Both are slower when the spacing is large, and when the time constant is plotted against the square of the diffusion distance (fringe spacing) an approximately linear dependence is observed at low spatial frequency. This indicates that both are diffusion process. It should be noted that the spatial frequency dependence, though measurable and repeatable, is only observable at lower spatial frequencies. This is probably due to polymerisation becoming the limiting factor as diffusion rate increases at the higher spatial frequencies.

b) Deterioration of acrylamide gratings

As described above, acrylamide gratings (i.e. those not containing significant proportions of crosslinker) deteriorate over a period of hours and days. This process is slower in gratings that have been dried in a dessicator and those that have a crosslinker in the formulation[22] which is indicative of a diffusion process and suggests that this deterioration could be a continuation of PP2. Figure 5 shows typical diffraction efficiency deterioration in the one-monomer formulation.

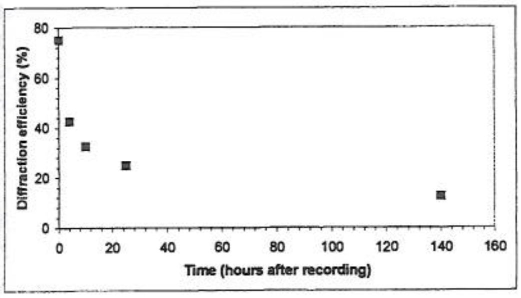


Fig. 5. The diffraction efficiency as a function of time after recording in a grating recorded in a photopolymer formulation containing no crosslinker

c) Role of diffusion in this material

For some time it has been clear that this material is one in which diffusion happens quickly and easily in comparison to most others[22]. So it is not so surprising that the monomer diffusion coefficient estimated for this material in the non crosslinking formulation is $D_0=1.61 \pm 0.03.10^{-7}cm^2/s$, which is significantly faster than other photopolymer systems. Some of our past work has indicated that diffusion occurs with ease over typical fringe widths. Studies of dye diffusion are a good example of this. Weak transmission gratings obtained when the formulation was prepared without any monomer were studied in order to quantify dye diffusion. The dye is a bigger molecule than acrylamide and bisacrylamide, but the diffusion was so fast that it could not be measured until the layers had been significantly modified (by reducing plasticizing TEA content) so that we were working with a much less permeable system. The linear dependence of time constant on fringe spacing was then obtained[25]. Another indicator of fast diffusion is the shape of the diffraction efficiency growth curve. Booth showed [2] that the shape of the DE growth curve in the DuPont photopolymer changed according to the relative speed of diffusion versus polymerization. There is a characteristic curve shape that occurs when polymerization is faster than diffusion, where an initial rapid increase is followed by a dip in efficiency and then a further, slower increase. The initial rapid increase is thought to occur because the polymerization occurs faster than the monomer can diffuse in. A continuous growth curve (where diffusion is thought to 'keep up' with polymerisation at all times) is only observed at high spatial frequencies in Booth's study. In our material this continuous type of curve is generally the only one observed although we have managed to observe the type shown by Booth by reducing both permeability of our layer and the spatial frequency of the gratings, and by using high recording intensity (in order of 100 mW/cm^2). This is shown in Figure 6, and is a further indication that diffusion is generally fast in our material. One of the most important indicators that diffusion is the primary process in the recording of gratings in this material is the fact that when gratings are post exposed with uniform illumination, they are not erased. In fact there is always a small increase in the DE under uniform exposure. Figure 7 is a typical example of the behaviour of gratings under uniform off Bragg post exposure. From this we must conclude that density change and not molecular polarizability change (i.e. bond conversion) is the main contributor to the diffraction efficiency observed in these gratings.

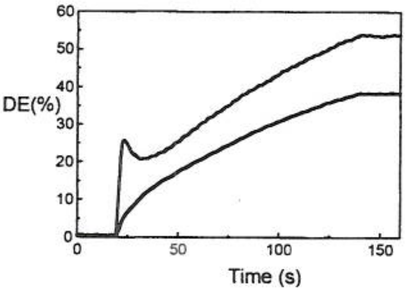


Fig. 6 Comparison of growth curves in gratings recorded in the standard formulation (lower line) and a reduced permeability binder (upper line) at 200 lines/mm

Any grating can actually be treated as the result of two gratings superimposed on each other, one due to local density change brought about by the diffusion that accompanies polymerization, and one due to local molecular polarizability change caused by the bond conversion that accompanies polymerization. Polymerization thus causes increased density and reduced molecular polarizibility[26] so these two gratings oppose each other. Since uniform off Bragg exposure of the grating will convert any remaining monomer to polymer across the whole grating, it will erase any refractive index modulation due to bond conversion (assuming that the initial exposure was moderate). If density modulation is the main contributing factor to diffraction efficiency in these gratings we would expect the diffraction efficiency of the grating to remain high after uniform exposure. If however, diffusion is restricted and density modulation is small, the bond conversion / molecular polarizibility would be the main contributing factor, and we would expect the diffraction efficiency of the grating to drop significantly as the remaining monomer is polymerized under uniform exposure. This allows us to determine the contribution that bond conversion makes to the overall grating by observing what happens when a grating is exposed to uniform intensity. Figure 7 shows that the grating is not erased under uniform exposure and a small increase in diffraction efficiency occurs.

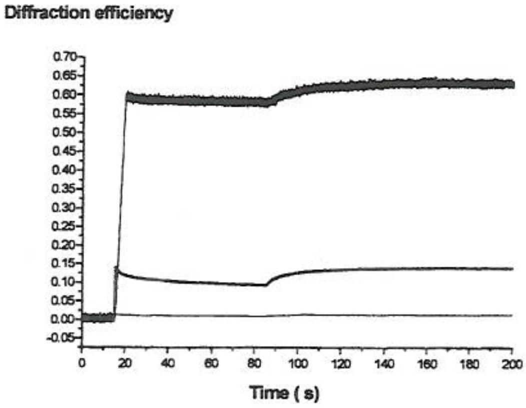


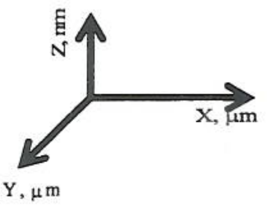
Fig. 7. Diffraction efficiency as a function of time for 1000 lines/mm gratings recorded in the normal way and then post exposed with a uniform beam, after a time interval of 70s. The initial exposures were 5s (upper curve) and 0.5 s (lower curve) at 9mW/cm^2.

The fact that the grating is not erased indicates that the contribution from the 'bond conversion' grating is small, and that the main contributor to grating diffraction efficiency is the density modulation. It is important to make this distinction because if the opposite were true, PP1 could be explained in terms of continued polymerization. Since density modulation is, in fact, the main contributing factor, PP1, which is a further increase in diffraction efficiency, is more likely to be due to further density increase as a result of diffusion.

d) direct observation of surface at boundary of illuminated area

A 198 μm × 260 μm area of the boundary between an illuminated area (a circle approx. 0.5 mm in diameter) and an unilluminated area (the surrounding dark area) was observed with the white light interferometer, at intervals from 5 to 1800 seconds. The results are shown in Figure 8. Within 5 second the material begins to swell at the border between an illuminated and unilluminated area. This would correspond to the movement of acrylamide monomer into the bright fringe area in a grating. This swelling in the illuminated area is observed routinely in gratings recorded in our material and has been reported on in detail in a recent publication[27]. Here it only occurs in the immediate vicinity of the border because the diffusion distances are larger than in a typical grating. What is interesting is that shortly after the initial swelling appears, a smaller amplitude raised area appears to the left of the initial swelling. The left of each picture is the area which was illuminated, so the smaller peak appears to be coming from the polymerized region and could be due to movement of material out of the polymerized area and in the opposite direction to the influx of monomer. Eventually (1800 seconds) the two waves are merged and one large peak is visible at the boundary.

This is a direct observation of the evolution of the swelling that occurs as a result of movement of material at the boundary between illuminated and unilluminated areas. The secondary peak, seen to appear from the left may be due to the movement of polymer molecules out of the illuminated area, corresponding to the flow of polymer into the dark fringes of a grating (PP2) .



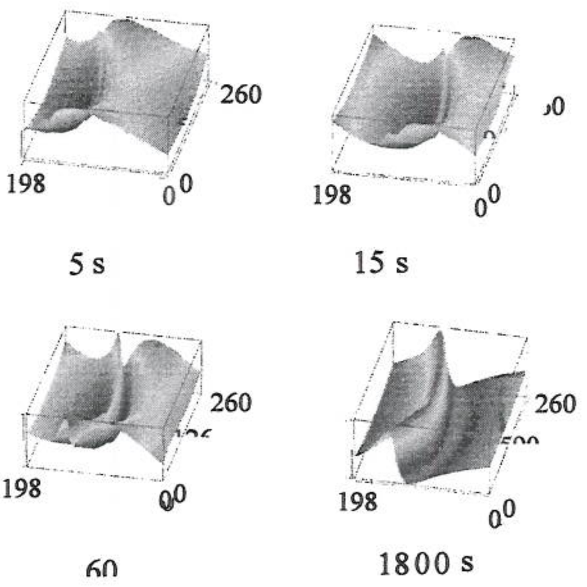


Fig. 8. Surface height profiles at the boundary of an illuminated circular area , 5, 15, 60 and 1800 seconds after (spatially uniform) exposure.

Each profile in Figure 8 shows the surface height variations across an 198 by 260 micron area at the boundary of the illuminated area. However, the vertical scale changes in each of the four pictures shown. It should also be noted that in this preliminary experiment it was not possible to ensure that the origin of each was at the same position in each of the four scans

CONCLUSIONS

Diffusion constants have been measured in the standard crosslinking formulation of the IEO photopolymer which are indicative of significantly faster diffusion than that occurring in the DuPont material. They are also significantly faster than those reported for very similar acrylamide based materials. A two way diffusion recording process is proposed which explains the two diffusion processes observed after short exposure, as well as the fall-off in diffraction efficiency observed in non crosslinked gratings. This involves both an influx of monomer into the polymerizing regions, and a flow of polymer molecules in the opposite direction. Additional supporting evidence is also outlined. It is also shown that diffusion, as opposed to bond conversion, is the main contributing process in the build up of grating diffraction efficiency in this material. Our improved understanding of the role of diffusion has already assisted in improvement of the material formulation and improved resolution and diffraction efficiency[28].

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